Laboratory Gas Ebullition Test Protocol
DRAFT – 1 September 2017

1) Establish chemical composition of the DNAPL sample provided by Brown and Caldwell. A DNAPL sample of 200 to 250 ml will be conveyed to the ERDC lab by Jacobs after picking up the sample from Brown and Caldwell. Characterization may have already been performed adequately by Brown and Caldwell, however we do not currently have these data. We will perform this analysis for this "batch" of DNAPL. It is important to know the relative proportion of VOC and PCB within the DNAPL. If the available DNAPL appears to have a higher VOC content than we believe is in the sediments, then we may want to adjust the DNAPL composition for the purposes of the study.

2) Column study will entail setting up an 8-inch diameter column with sediment and cap material (using the presumed cap design at the time of testing). The general design of the column test will entail construction of a the column with the following materials, starting from the bottom of the column:
    a. at least 1 cm of small gravel/coarse sand
    b. approximately 6-inch layer of Harbor mud/sediment;
    c. cap materials atop the sediment; and
    d. 6 to 12-inch water column above the top of the cap.

    When adding water to the columns, use synthetic seawater, adjusted for salinity appropriate for the river/New Bedford harbor.

3) Set up two columns, one from a heavily contaminated portion of the sediment with higher gas ebullition rates (based on field observations), and one from another, less contaminated location. After the columns are set up and "packed", let the columns rest for at least one day to allow the sediment to consolidate due to the weight of the cap materials.

4) *Phase 1*: Initial 8-inch column test: pump air through the column at the field ebullition rate or a prescribed rate and observe whether NAPL becomes apparent in the water above the top of the cap (minimum of 7 days – up to 14 days). If there is a sheen apparent in the water during this time, collect a water sample for analysis for PCBs and VOCs and TOC. If there is no sheen, at the end of this step (i.e., 7 days), collect a water sample for PCBs and VOCs and TOC.

    a. Test ERDC in-house TOC analyzer to determine whether the detection limits are suitable for our needs (e.g., DL < 100 ug/L? or < 10ug/L).
    b. Test Modernwater RaPID Assay (or equivalent) immunoassay test kit (see attached cut-sheet) for PCBs. Relatively immediate results from a "field" test will greatly aid decision making during the study. Compare immunoassay results with TOC results.

5) *Phase 1b*: Parallel test -- Bromide tracer (and possibly methylene blue dye) test in a 4-inch column with a smaller thickness (3-inch) of sediment and a cap and measure/observe appearance of the tracer in the water overlying the cap during air pumping (it is important to determine when the dye/tracer appears in the water overlying the "cap"). Run this gas ebullition (i.e., air pumping) for up to 30 days. Measure bromide using an ion-selective probe. This will

help us determine an enhanced diffusion rate constant for the sediment.

6) *Phase 2*: Perform 2nd 8-inch column test: Using established columns, inject DNAPL from the site into the sediment above the gas distribution apparatus (using a syringe and ports already present in the column) and observe whether NAPL appear in the water above the cap during air/gas pumping. Run test for a minimum of 7, but up to 14 days. Also add bromide tracer (and/or methylene blue dye) and measure/observe appearance of the tracer in the water overlying the cap. If there is a sheen apparent in the water during this time, collect a water sample for analysis for PCBs and VOCs and TOC. If there is no sheen, collect a sample for PCBs and VOCs (and possibly TOC) after 7 days OR upon observation of the tracer. At the end of this step (e.g., 14 days), collect a water sample for PCBs and VOCs and also TOC and/or immunoassay field testing. Depending on what we observe, we will collect between two and four samples each for laboratory analysis of VOCs and PCBs.

7) *Phase 3*: IF no clear evidence of transport due to ebullition only, then we will test the combination of ebullition and groundwater advection → Groundwater flow upward through the column will be set to the velocity determined by the groundwater flux field data collected in the river in the September 2017 field program, or if the results from the field program are not available before this column testing, then a simulated groundwater velocity of 1×10^{-5} cm/sec will be used for the test (1×10^{-5} cm/sec = 0.86 cm/day).[1] During this test of combined groundwater advection and gas ebullition, the water above the top of the cap will be monitored for the appearance of NAPL. The test will run for a minimum of 7 days and up to 14 days. Water used for the advection test will be synthetic seawater made in the ERDC lab. The salinity of the water will reflect the salinity of the river/harbor water from alongside the AVX site. If there is a sheen apparent in the water above the cap during this time, collect a water sample for analysis for PCBs and VOCs and TOC. If there is no sheen, collect a sample for PCBs and VOCs and TOC after 7 days OR upon observation of the tracer. At the end of this step (e.g., 14 days), collect a water sample for PCBs and VOCs and also TOC and/or immunoassay PCB measurement. Depending on what we observe, we will collect between two and four samples each for laboratory analysis of VOCs and PCBs

8) *Phase 4:* if NAPL or significantly elevated TOC is present in the water column from ebullition or ebullition in the presence of groundwater advection; modify the cap by adding organoclay and/or activated carbon. Test using gas ebullition AND groundwater advection (this will simulate the "worst" case). Repeat the testing described for Phase 3.

9) If no DNAPL has been observed in the water above the cap in the last test phase, (i.e., either Phase 3 or Phase 4), disassemble and "section" the cap materials to determine the degree of migration of PCBs and VOCs up into the cap after the test period. Particular emphasis will be collection of solids along any clear preferential paths that have formed for gas bubbles through the cap materials. This will involve laboratory analytical testing of the solids. Analysis can be

[1] Groundwater velocity will be estimated using measured head differences within the river bottom sediments and porosity of samples collected during the September 2017 field program. River bottom permeability estimates will be based on previously measurements.

performed in an ERDC laboratory (not in the sediment lab where the columns will be) or we can have the solids samples shipped to the lab of our choosing. The volume available for each solids sample will be small, which will impact the detection limit for each sample. However, we are looking for ppm levels or greater contamination.

Notes about the analytical methods used in this study:

- Lab detection limit for dissolved PCBs should be ~ 1 ug/L (or lower). This limit was determined by considering the impact of a microliter of NAPL migrating through the cap and the resulting dissolved concentration in 12 inches of water above the cap in the 8-inch column.
- Lab DL for sediment PCBs should be 1 mg/L or less.
- Standard 8240 lab protocols for VOCs.
- Modernwater immunoassay or equivalent to aid decision making in ERDC lab. Modernwater RaPID Assay (immunoassay for dissolved PCBs -- nominal range 0.25 to 5.0 ppb total PCBs as Aroclor 1254. Modernwater RaPID Assay (immunoassay for soil PCBs -- nominal range 0.5 to 10 ppm total PCBs as Aroclor 1254.
- Test in-lab ERDC TOC analysis for utility for seeing "breakthrough" of COCs into water above cap. TOC detection limit being confirmed.
- Bromide (and possibly methylene blue) tracer to understand enhanced diffusion rates. Bromide is more sensitive analysis and easily performed using an ion selective probe that ERDC has available.

Table of Analyses						
	Media	**PCBs**		**VOCs**	**TOC**	**Bromide**
		Screen**	**Lab**	**Lab**		
Pre-test*	DNAPL:	0	1	1	1	0
	Water	0	0	0	1	0
	Solids (cap &or sediment)	0	0	0	1	0
Phase 1	Water	4	2	2	4 to 8	0
	Solids	0	0	0	0	0
Phase 1b	Water	0	0	0	0	Many
	Solids	0	0	0	0	0
Phase 2	Water	4	2	2	4 to 8	Many
	Solids	0	0	0	0	0
Phase 3	Water	4	2	2	4 to 8	0
	Solids	0	0	0	0	0
Phase 4	Water	4	2	2	4 to 8	Many
	Cap material / Solids***	5 to 10	5	5	4 to 8	0

* Assume sediment is already characterized for PCBs and VOCs

** Screen -- using Modernwater RaPID Assay (immunoassay for dissolved PCBs -- nominal range 0.25 to 5.0 ppb total PCBs as Aroclor 1254

*** Solids Screen -- using Modernwater RaPID Assay (immunoassay for soil PCBs -- nominal range 0.5 to 10 ppm total PCBs as Aroclor 1254

Estimated costs:

- The final cost will, of course depend on what we do, these do not include analytics.

Setup Column 1:	$7K
Setup column 2:	$7K
Setup column 3; 4 inch column	$3K
Run Phase 1 test:	$2K
Run Phase 2 test:	$2K
Run Phase 3 test:	$2K
Run Phase 4 test:	$3K
Modify cap:	$3.5K per column ($7K)

Breakdown, cleanup, and disposal: $7K

Replacement Cost $20K (if both columns need to be replaced; $10K per column)

Total without replacement cost: $40K

Total with replacement cost: $60K